

METAL NANOTUBULE MEMBRANES WITH ELECTROCHEMICALLY SWITCHABLE ION-TRANSPORT SELECTIVITY

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Abstract

Membranes that contain cylindrical metal nanotubules that span the complete thickness of the membrane are described. The inside radius of the nanotubules can be varied at will; nanotube radii as small as 0.8 nm are reported here. These metal nanotubule membranes show selective ion transport analogous to that observed in ion-exchange polymers. Ion permselectivity is observed because excess charge density can be present on the inner walls of the metal tubules. The membranes reject ions of the same sign, and transport ions of the opposite sign, as this excess charge. Because the sign of the excess charge on the tubule can be changed potentiostatically, a metal nanotubule membrane can be either cation selective or anion selective, depending on the potential applied to the membrane.

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A variety of materials that contain pores of molecular dimensions are known including the porin proteins (1,2), zeolites (3), and fullerene tubules (4). Synthetic membranes with monodisperse pores that approach molecular dimensions might be useful as mimics for the biological systems and would be useful in membrane science and technology. In this report, we introduce a new class of membranes that contain cylindrical nanoscopic metal tubules that run the complete width of the membrane. These metal nanotubule membranes show selective ion-transport analogous to that observed in ion-exchange polymers (5). Ion permselectivity (6) occurs because excess charge density can be present on the inner walls of the tubules. The tubes reject ions of the same sign, and transport ions of the opposite sign, as this excess charge. This is only possible when the inside radius of the tubule is small relative to the thickness of the electrical double layer (7) within the tubule. These membrane can be either cation selective or anion selective, depending on the potential applied to the membrane. Hence, these metal nanotubule membranes can be viewed as universal ion exchange membranes.

The pores in a commercially available polycarbonate filtration membrane (Poretics) were used as templates (8) to form the metal (gold) nanotubules. These membranes contain cylindrical nanopores of uniform radius (25 nm, 6×10^8 pores per cm^2) that run through the complete thickness (6 μm) of the membrane. Gold was electrolessly plated (9) onto the walls of these pores to yield a gold nanotubule within each pore (Fig. 1). Gold films are also deposited on both faces of the membrane. These gold surface layers allow us to make electrical contact to the nanotubules within the pores. The thickness of the gold layers deposited on the pore walls can be controlled by varying the plating time. As a result, the inside radius of the gold nanotubules can be varied at will (as

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determined from measurements of gas (He) flux (10) across the tubule-containing membrane).

We describe the results of three sets of experiments that demonstrate that these metal nanotubule membranes can show selective ion transport. All of these experiments involve a U-tube cell in which the membrane to be studied separates two aqueous solutions. The simplest experiment entails using a "feed" solution of a colored anionic or cationic species on one side of the membrane and a "receiver" solution that is initially devoid of the colored species on the other side of the membrane. A membrane that contained ~ 2.5 nm radii (10) Au nanotubules was used for these experiments.

When the feed solution is 1 mM in KCl and 0.5 mM in the cationic dye methylene blue, and the receiver solution is 1 mM KCl, the initially-colorless receiver solution turns blue due to transport of the cationic dye across the membrane (Fig. 2). In contrast, when the feed solution is 1 mM in KCl and 5 mM in KMnO₄ (MnO₄⁻ is red), and the receiver solution is 1 mM KCl, the receiver solution remains colorless (Fig. 2). These experiments provide simple visual evidence that this membrane transports a large cation but does not transport a much smaller anion. We have used potentiometric measurements to explore the nature of this cation permselectivity.

The extent of ion permselectivity displayed by a membrane can be expressed quantitatively by the transference numbers (11) for cations (t_+) and anions (t_-) within the membrane. Transference numbers can be determined potentiometrically by using a concentration cell (11), in which the membrane to be evaluated separates two electrolyte solutions that contain the same salt but at different concentrations. For a 1:1 salt, the membrane potential (E_m) is given by

$$E_m = (2.303RT/nF)(t_+ - t_-) \log(a_h/a_l) \quad (1)$$

where a_h and a_l are the activities of the salt in the solution of high and low salt concentration, respectively (6). Eq. 1 indicates that for an ideal cation-permselective membrane ($t_+ = 1.0$ and $t_- = 0.0$), a plot of E_m versus $\log(a_h/a_l)$ would be linear with an intercept of 0 and a slope of 59 mV (dashed line, Fig. 3).

A concentration cell was assembled in which a gold-nanotubule membrane separated two KCl solutions. The potential of the membrane was not controlled with a potentiostat. However, Cl^- adsorbs strongly to gold (12), and the gold films on the membrane faces and the inside walls of the gold tubules have excess negative (Cl^-) charge on their surfaces. This excess negative charge is balanced by a layer of excess positive charge (K^+) in the solution immediately adjacent to gold surfaces (the electrical double layer) (7).

Data obtained from this concentration cell, for gold nanotubule membranes prepared for various plating times (Fig. 3), show that these membranes can show ideal cation-permselective behavior and that the region over which ideal behavior is observed is extended to higher salt concentrations (on the high concentration side of the membrane) as plating time increases. These observations can be explained as follows: Over the range of plating times used in Fig. 3, the average inside radii of the gold tubules varied from ~ 9.4 nm (60 min plating time) to ~ 0.8 nm (180 min plating time) (10). Gouy-Chapman theory (7) predicts that over the salt concentration range used here, the thickness of the electrical double layer within the tubules (as approximated by the Debye length) varies from ~ 30 nm (lowest concentration) to ~ 0.3 nm (highest concentration). Fig. 3 indicates that the gold nanotubule membranes show ideal cation permselectivity, provided the radius of the tubule is small relative to the thickness of the electrical double layer within the tubule.

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To illustrate this point, consider the membrane plated for 60 min. The tubules in this membrane are on average ~ 9.4 nm in inside radius. At low concentrations of salt, the electrical double layer should be thicker than this tubule radius. Anions are excluded from the tubes, and ideal cation permselectivity is observed. At high salt concentrations, the electrical double layer is thin relative to the tubule radius. Anions can now enter the tubules and ideal cation permselectivity is lost (Fig. 3). Finally, the membrane plated for 180 min shows cation permselectivity almost identical to that of the ionomer Nafion® (13), which is a highly cation-permselective polymer used in industrial electrolytic processes (5).

We consider now the idea of controlling the permselectivity by potentiostatically injecting excess charge into the gold nanotubules. For these studies, it is essential to use an anion that does not adsorb to gold because we do not want the excess charge to be determined by adsorption. Because F⁻ does not adsorb to Au (14), KF was chosen as the electrolyte. A concentration cell was assembled in which a gold nanotubule membrane separated solutions that were 1 mM and 10 mM in KF. This membrane was connected (through the Au surface layers) to the working electrode lead of a potentiostat and the potential applied to the membrane was varied over the range from -0.5 V to + 0.5 V versus Ag/AgCl. The E_m values were measured at each applied potential (Fig. 4).

The dashed lines at the top and bottom of Fig. 4 are the E_m values that would be achieved if the nanotubule membrane showed ideal cation and ideal anion permselectivity, respectively (Eq. 1). At negative applied potentials, the nanotubule membrane shows ideal cation permselectivity, whereas at positive applied potentials the membrane shows ideal cation permselectivity. This

selectivity occurs because at negative applied potentials, excess electrons are present on the walls of the tubes, and excess positive charge (K^+) accumulates within the tubes. As a result, anions (F^-) are excluded and cations (K^+) are transported by the membrane. At positive applied potentials the opposite situation occurs, and cations are excluded and anions are transported.

For any combination of metal and electrolyte, there is a potential called the potential of zero charge (pzc) where there is no excess charge on the metal. At this potential the nanotubule membranes should show neither cation nor anion permselectivity, and E_m should approach (15) 0 mV. E_m for the tubule-containing membrane does, indeed, go from the ideal cation permselective value, through zero to the ideal anion permselective value (Fig. 4). Furthermore, the potential at which E_m approaches (15) zero is close to the reported pzc [-4 mV for Au in 1 mM NaF (16)].

Fig. 4 shows that the gold nanotubule membranes can function as electronically switchable ion exchange membranes. However, it would seem that this would only be possible if the electrolyte contained only nonadsorbing anions such as F^- . If an adsorbing anion (such as Cl^- or Br^-) (12,17) were present, it would adsorb at positive applied potentials yielding a cation permselective membrane. While the anion would not adsorb at sufficiently negative applied potentials, the metal would have excess electron density at such potentials, and, again, cation permselectivity would be observed. Hence, in the presence of an adsorbing anion, cation permselectivity will be observed at all applied potentials (Fig. 5, upper curve).

Anion adsorption can be prevented by adsorbing a monolayer of a strongly adherent thiol molecule to the Au surfaces (18,19). 1-Propanethiol (PT) was used here because the gold nanotubules can still be wetted with water

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after adsorption of the PT monolayer (19). The E_m versus applied potential curves for an untreated and PT-treated gold nanotubule membrane, with KBr solutions present on either side of the membrane, are shown in Fig. 5. The untreated membrane shows only cation permselectivity, but the permselectivity of the PT-treated membrane can be switched, exactly as was the case with the nonadsorbing electrolyte (Fig. 4).

We have demonstrated that these metal nanotubule membranes can be cation permselective, anion permselective or nonselective, depending on the potential applied to the membrane (20). These membranes can be as permselective as the commercially relevant Nafion® polymer and should have applications in both fundamental and applied electrochemistry. In addition, because the gold tubules have radii that approach molecular dimensions, these membranes might have applications in chemical separations, for example, industrial gas separations (21).

REFERENCES AND NOTES

1. M. Hofnung, *Science*, **267**, 473 (1995).
2. T. Schirmer, T.A. Keller, Y.-F. Wang, and J.P. Rosenbusch, *Science*, **267**, 512 (1995).
3. J.S. Beck, *et al.*, *J. Am. Chem. Soc.* **114**, 10834 (1992).
4. E. Dujardin, T.W. Ebbesen, H. Hiura, and K. Tanigaki, *Science*, **265**, 1850 (1994).
5. R. L. Dotson and K. E. Woodard, in *Perfluorinated Ionomer Membranes*, A. Eisenberg and H.L. Yeager, Eds. Vol. 180 of the ACS Symposium Series, (American Chemical Society, Washington DC, 1982).

Nishizawa et al.

6. J. Koryta, *Ion-Selective Electrodes* (Cambridge Univ. Press, Cambridge, 1975), pp. 21-23.
7. A. J. Bard and L. R. Faulkner, *Electrochemical Methods* (Wiley, New York, 1980), pp. 500-515.
8. C. R. Martin, *Science*, **266**, 1961, 1994.
9. V. P. Menon and C. R. Martin, *Anal. Chem.*, submitted.
10. See W. J. Petzny and J. A. Quinn, *Science* **166**, 751 (1969); C. Liu, Ph.D. Dissertation, Texas A & M University, (College Station, TX 1991). This method provides the average pore size. However, if pores significantly larger than the average were present, the membranes would not be permselective.
11. N. Lakshminarayanaiah, *Transport Phenomena in Membranes* (Academic Press, New York, 1969), chap. 3.
12. S. Biggs, P. Mulvaney, C. F. Zukoski, F. Grieser, *J. Am. Chem. Soc.* **116**, 9150 (1994)
13. C. Liu and C. R. Martin, *J. Electrochem. Soc.* **137**, 3114 (1990).
14. D. L. Rath and W. N. Hansen, *Surf. Sci.* **136**, 195 (1984).
15. In fact, at the pzc, the membrane should show the liquid junction potential (11) based on the transference numbers of the ions in the bulk solution.
16. J. Clavilier and C. N. V. Huong, *J. Electroanal. Chem.* **80**, 101 (1977). This reported pzc is for polycrystalline Au. Electrochemists may debate the precise meaning of the pzc for a polycrystalline metal surface. However, for the purposes of this paper, it is the potential at which there is no net excess charge on the polycrystalline metal surface.
17. M. R. Deakin, T. T. Li, O. R. Melroy, *ibid.* **243**, 343 (1988).

Nishizawa et al.

18. A. Ulman, *An Introduction to Ultrathin Organic Films from Langmuir-Blodgett to Self-Assembly* (Academic Press, San Diego, 1991).
19. This is undoubtedly because prior studies have shown that because of its short alkyl chain, PT monolayers are disordered. See C. D. Bain, E. B. Troughton, Y.-T. Tao, J. Evall, G. M. Whitesides, R. G. Nuzzo, *J. Am. Chem. Soc.* **111**, 321 (1989).
20. Although polymeric membranes that show switchable transport properties have been described [see, for example, P. Burgmayer and R. W. Murray, *J. Phys. Chem.* **88**, 2515 (1984)], the switchability was based on faradaic electrolysis of the polymer.
21. J. M. S. Hennis and M. K. Tripodi, *Science* **220**, 11 (1983).
22. J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, (Plenum, New York, 1970), vol. 1, p. 211.
23. *Handbook of Chemistry and Physics*, R. C. Weast, Ed. (CRC Press, Boca Raton, 1988), p. D169.
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FIGURE CAPTIONS

Fig. 1. (A) Schematic diagram of electroless Au plating procedure. (B) Transmission electron micrograph showing a cross section of an Au-nanotubule membrane. The Au tubules are the black rings. The elliptical appearance is caused by the microtoming process. Plating time was 10 min.

Fig 2. Absorption spectra of receiver solutions after 36 hour permeation experiments with the methylene blue cation in the feed solution (upper spectrum) and the permanganate anion in the feed solution (lower spectrum).

Fig. 3. E_m values obtained for membranes prepared for the indicated plating times. The solution on the I side of the membrane was 0.1 mM KCl. The solution on the h side of the membrane was varied from 0.1 mM KCl to 1 M KCl. The E_m values were measured by using two Ag/AgCl (KCl saturated) electrodes placed in each half-cell through agar salt-bridges. Mean activities were calculated from Debye-Hückel theory (22) (< 0.1 M) and from reported activity coefficients (23) (\geq 0.1 M). The dashed line is for ideal cation-permselective behavior (Eq. 1, $t_+ = 1$ and $t_- = 0$).

Fig. 4. Variation of E_m with potential applied to the membrane (1 mM KF on the I side, and 10 mM KF on the h side, of the membrane; tubule radius ~1.1 nm). Electrical contact was made to the membrane by sandwiching it between two copper foils that have a conductive adhesive. The Cu was masked with plastic adhesive tape and epoxy. Immediately prior to measurement, the membranes were cathodically cleaned (stripped of adsorbed ions) by holding the potential at -0.5 V versus Ag/AgCl for 10 min in 50 mM KF solution. The potential of the membrane was controlled with a potentiostat versus a Ag/AgCl reference electrode immersed in the side-h solution. E_m was measured with

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the membrane under potential control.

Fig. 5. Variation of E_m with potential applied to the membrane (1 mM KBr on I side and 10 mM KBr on h side; membrane as per Fig. 4) for (A) an untreated Au nanotubule membrane and (B) a PT-coated membrane. The self-assembly of the PT molecules to the Au surfaces was conducted by immersion of the membrane in ~ 1 mM propanethiol (in ethanol) for 24 hours followed by careful rinsing with pure ethanol and water.

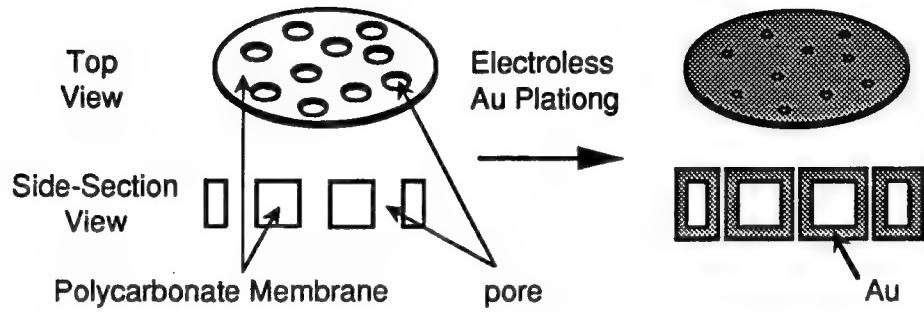


Fig. 1A

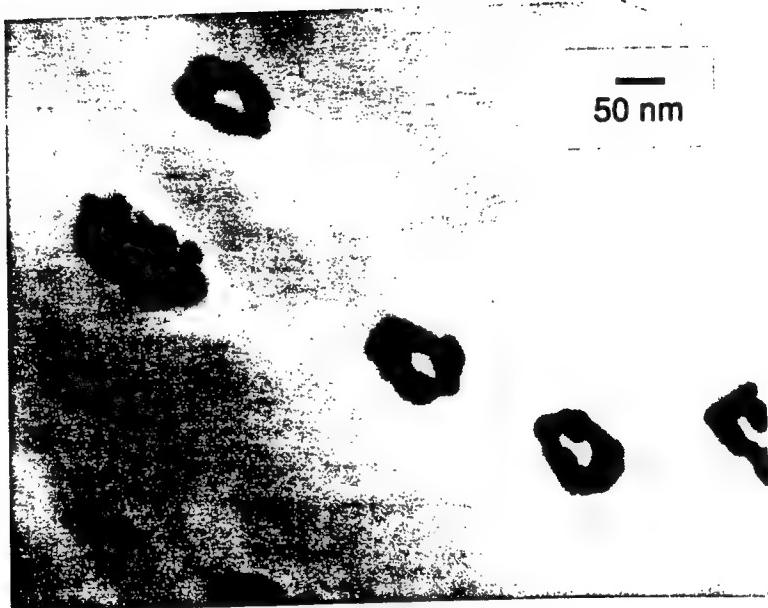
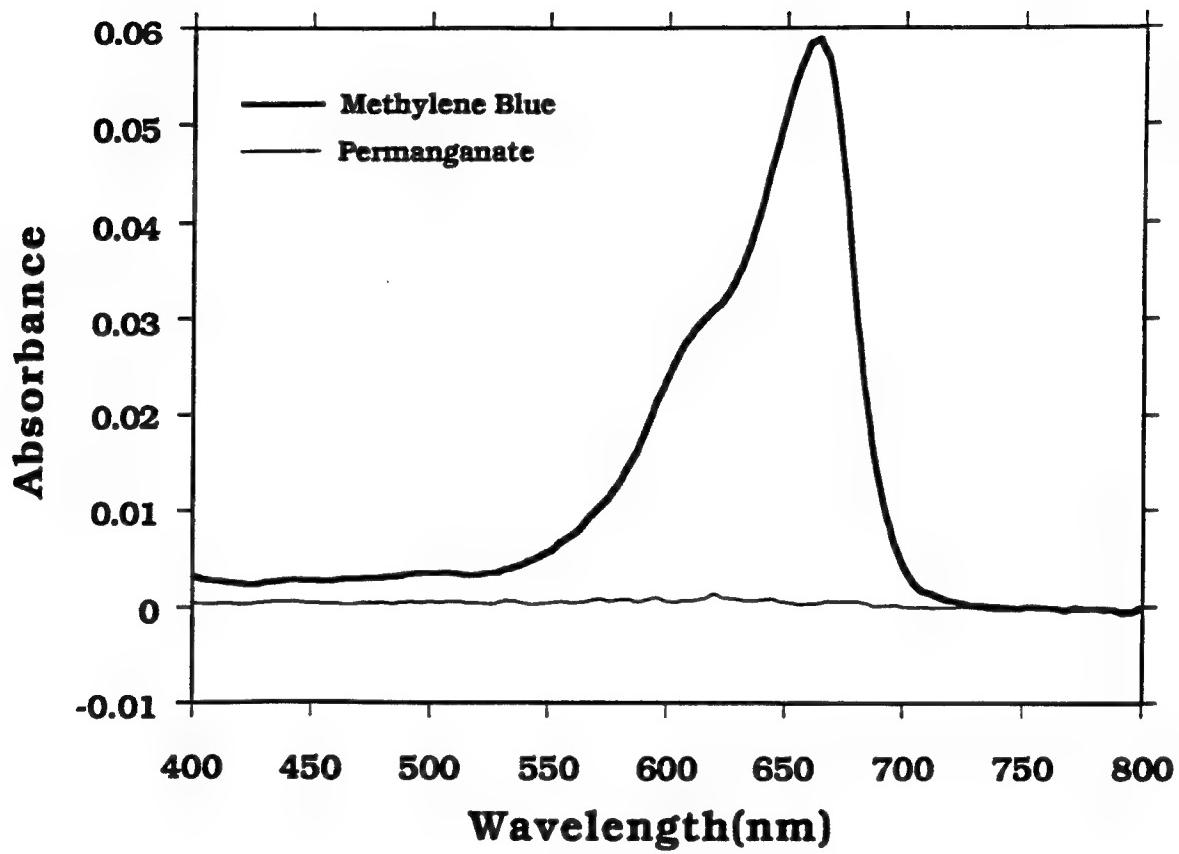


Fig 1B



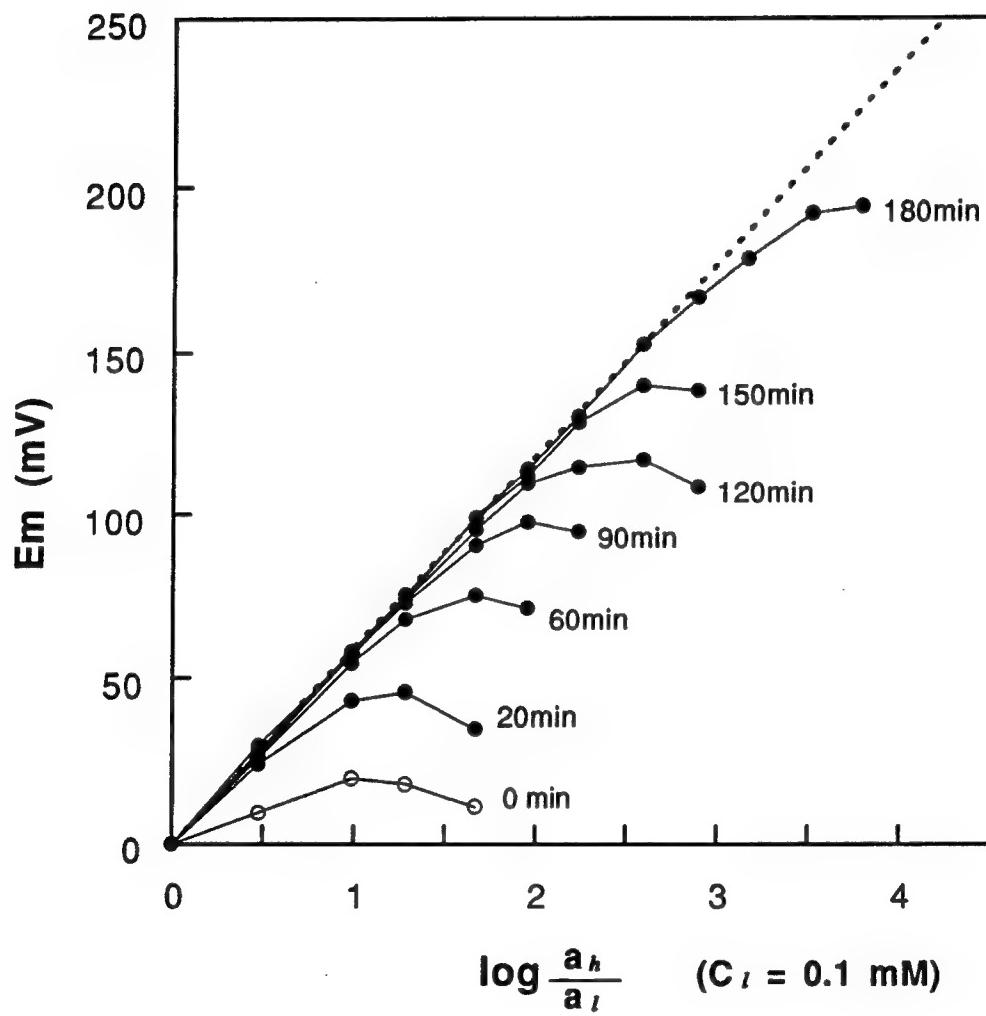
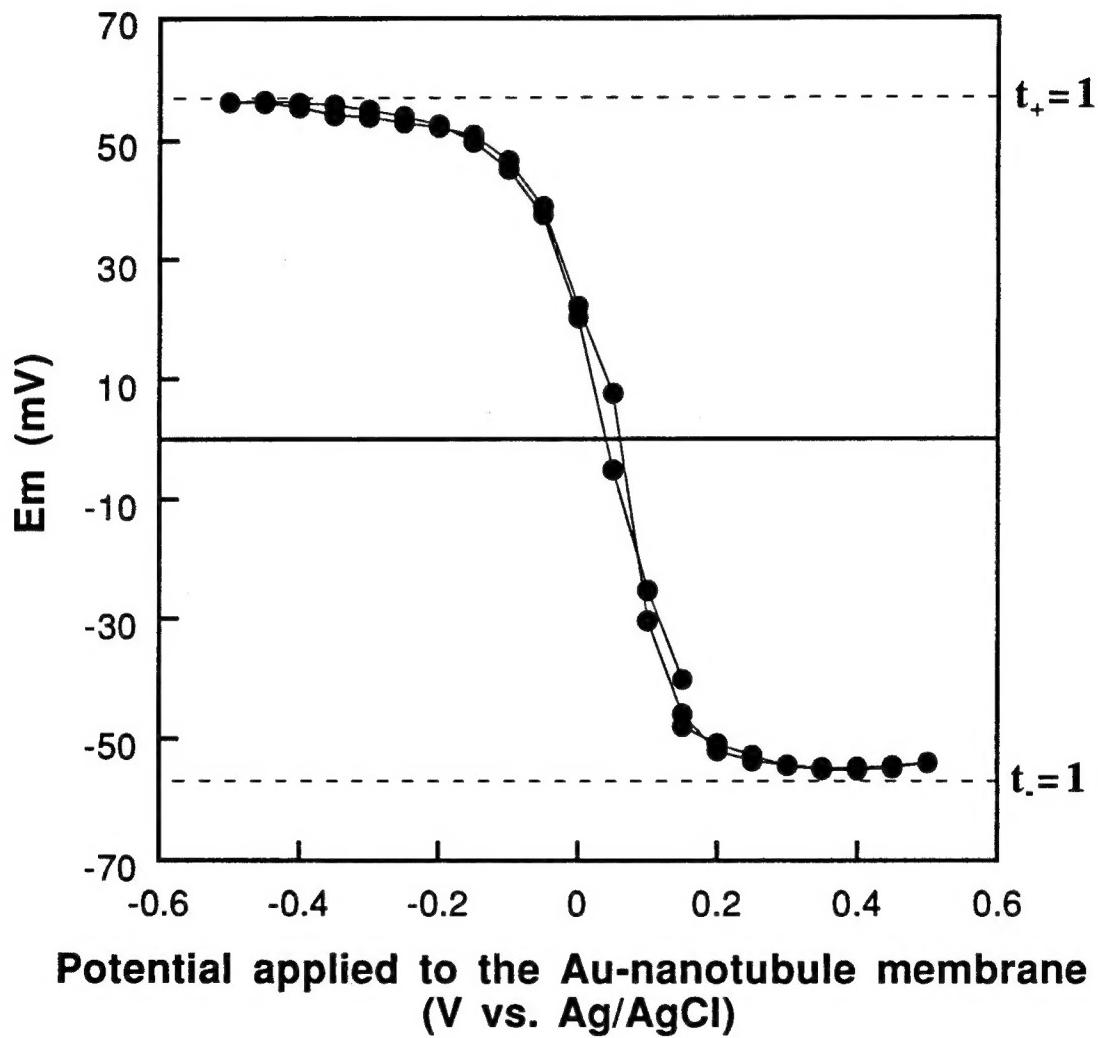
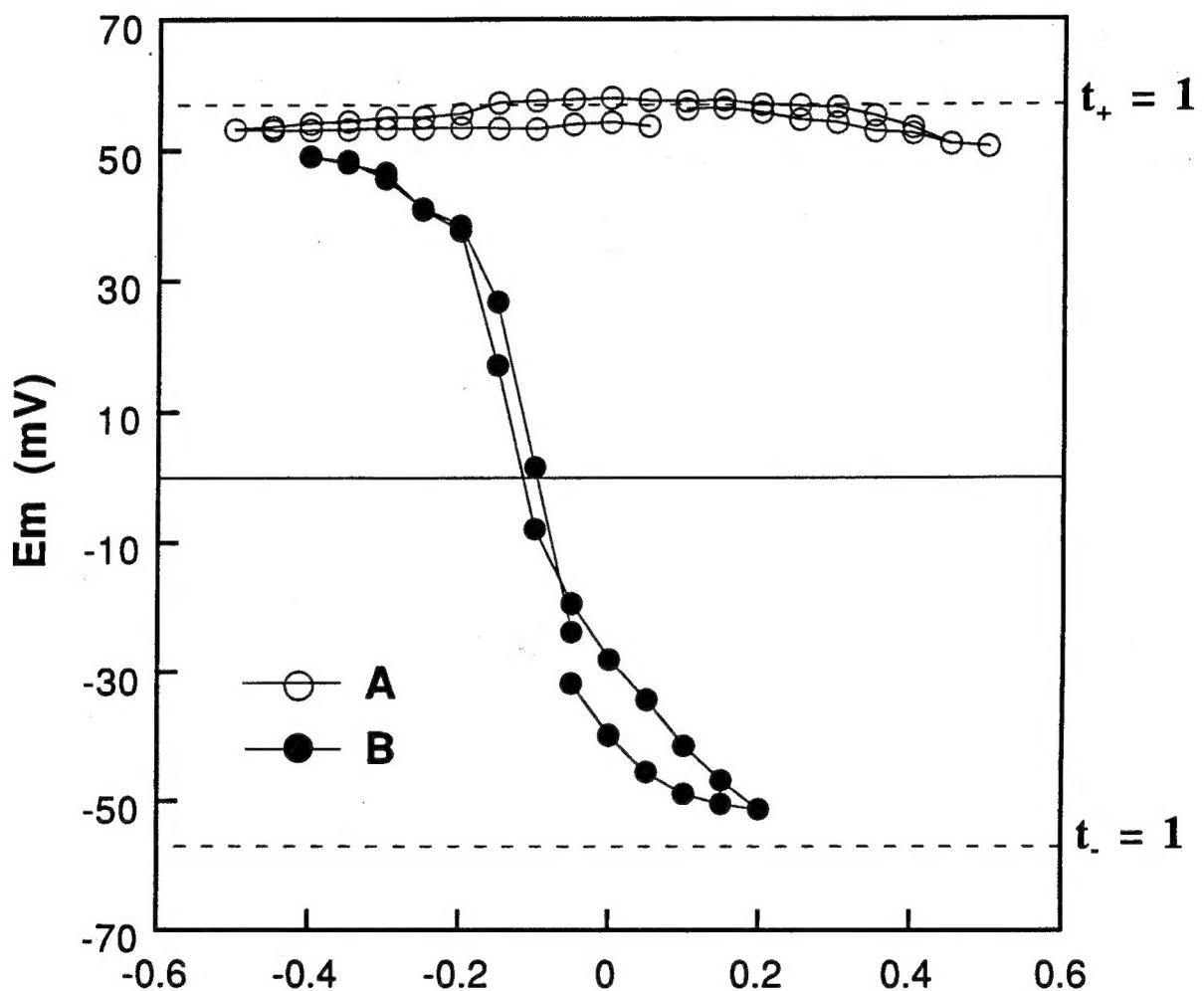


Fig. 2





Potential applied to the Au-nanotubule membrane
(V vs. Ag/AgCl)

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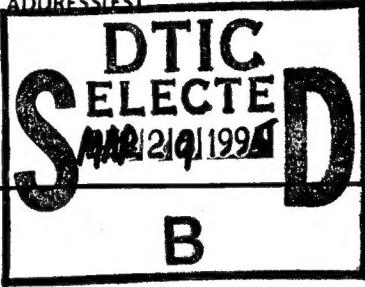
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